



	Experiment title: An Insight in to Zinc Exchangeability in Soils using EXAFS to Define Kinetic Exchange Parameters	Experiment number: ME-741
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Report:

Introduction

With past and present industrial developments throughout the world, Zn contaminants in soils continue to raise concerns for both governments and industry. An accurate assessment of Zn contamination in soils is commonly based on the degree of availability to organisms within an ecosystem. The implementation of isotopic exchange methods has proven to be a useful tool in assessing Zn availability in soils. The underlying assumption of these methods is that the exchangeable Zn correlates to the available Zn in soils. Even with this assumption, limitations exist in understanding the mechanisms controlling availability and exchangeability that can only be clarified through identification of the Zn species involved in the process.

The objective of this study was to identify the major Zn species, in terms of coordination chemistry, present in the exchangeable fraction of two smelter polluted soils. The soils selected for this study were chosen due to their high Zn content and their extreme differences in characteristics. The Dornach (Switzerland) soil is highly organic and calcareous with a total Zn concentration of 1685 mg Zn kg⁻¹ soil. The Mortagne (France) soil is low in organics and slightly acidic with 1300 mg Zn kg⁻¹ soil.

As a precursor to this study, experiments were performed to identify the soil exchangeable Zn pools using two independent methods. The first method was the isotopic exchange kinetic (IEK) method as described by Sinaj *et al.* (1999) and the second method was a selective sequential extraction (SSE) performed on ⁶⁵Zn labeled soils incubated for 120 days (Diesing *et al.*, in submission) The 120-day IEK estimate of the exchangeable Zn was 768 and 658 mg Zn kg⁻¹ soil for the Dornach and Mortagne soils, and are consistent with the SSE exchangeable Zn quantification. Additionally, the SSE highlighted the most exchangeable Zn pool residing in the first three fractions (F1, F2, F3) as indicated by the highest levels of specific activity (SA) with no significant difference in SA between the fractions. Zn speciation of the untreated soils and extraction residues associated with the exchangeable pool were studied by EXAFS on nonlabeled Dornach and Mortagne soils. The results of this portion of the study are presented in this report.

Methods

The soils were ground to a fine powder and subjected to a six-step (F1-F6) SSE developed by Salbu *et al.* (1998) with the extractants shown in Table 1. The chemical extraction procedure is designed to remove metals in a step-wise fashion first from weak outer-sphere bound forms (F1-F3), then from tightly bound outer- and inner-sphere complexes (F4 and F5) and finally from crystalline metal forms (F6). After each extraction step the residue was removed from the SSE procedure, air-dried at 35° C, reground and pressed into a 5 mm pellet for EXAFS analysis.

F1	H ₂ O
F2	1 M NH ₄ OAc, pH 7
F3	1 M NH ₄ OAc, pH 5 (HNO ₃)
F4	0.04 M NH ₂ OH-HCL in 25% CH ₃ COOH
F5	30% H ₂ O ₂ , pH 2 (HNO ₃) followed by 3.2M NH ₄ OAc in 20% HNO ₃
F6	7 M HNO ₃

Table 1. Selective sequential extraction (Salbu *et al.*, 1998) chemical extractants used in this study.

Zn K-edge spectra were recorded on the Dornach and Mortagne bulk samples and key SSE residues including Mortagne F2 and F3, and Dornach F3 through F5 using a diode in fluorescence mode. EXAFS data analysis was done by linear combination fits (LCF) using the Zn K-edge reference spectra library described by Manceau *et al.* (2003). The number of components for the fit of the SSE residue and soil spectra was constrained to four since the precision of the method does not enable a reliable quantification of more complex mixtures. From the percentages of the four components, Zn species concentrations (mg Zn kg⁻¹ soil) were calculated in each sample by multiplying the percentage of each component by the total Zn concentration in the given sample.

Results

The set of Zn EXAFS spectra for the Dornach untreated soil and SSE residues were simulated by a combination of the following reference spectra in varying proportions: Zn-sorbed phyllosilicate, Zn-sorbed birnessite and Zn-humic acid complex (Zn-HA) at low and high Zn loading. Fits of equivalent quality were obtained between Zn-HA at high Zn loading and by aqueous Zn allowing these species to be considered as representatives for weakly bound inner sphere Zn-organic complexes and outer sphere complexes (Sarret *et al.*, 1997) and are referred to as "octahedral Zn-HA and/or outer sphere complexes". Likewise, Zn-HA at low Zn loading could be replaced by Zn-sorbed ferrihydrite since both compounds are tetrahedrally coordinated with Zn and are further noted as "tetrahedral Zn-HA and/or Zn-sorbed ferrihydrite". The normalized sum-square ranged from 0.03 to 0.2 with the best fit for the untreated soil spectra followed by each successive extraction with decreasing accuracy.

Figure 1B shows that the octahedral Zn-HA and/or outer sphere complexes dominate in the Dornach soil (57%) followed by Zn species sorbed to phyllosilicates (30%), by tetrahedral Zn-HA and/or Zn-sorbed ferrihydrite (17%) with no indication of Zn associated to Mn oxides (birnessite). Although the mean value changes in species distribution between F3 residue (DF3) and the untreated soil (DRef) appear substantial, only the difference in octahedral Zn-HA and/or outer sphere complexes is significant when considering the precision of the method ($\pm 10\%$ of total Zn). However, the decrease of Zn-sorbed phyllosilicates in DF4 and DF5 compared to the untreated soil is significant. These results, in addition to IEK and extracted/⁶⁵Zn labeled

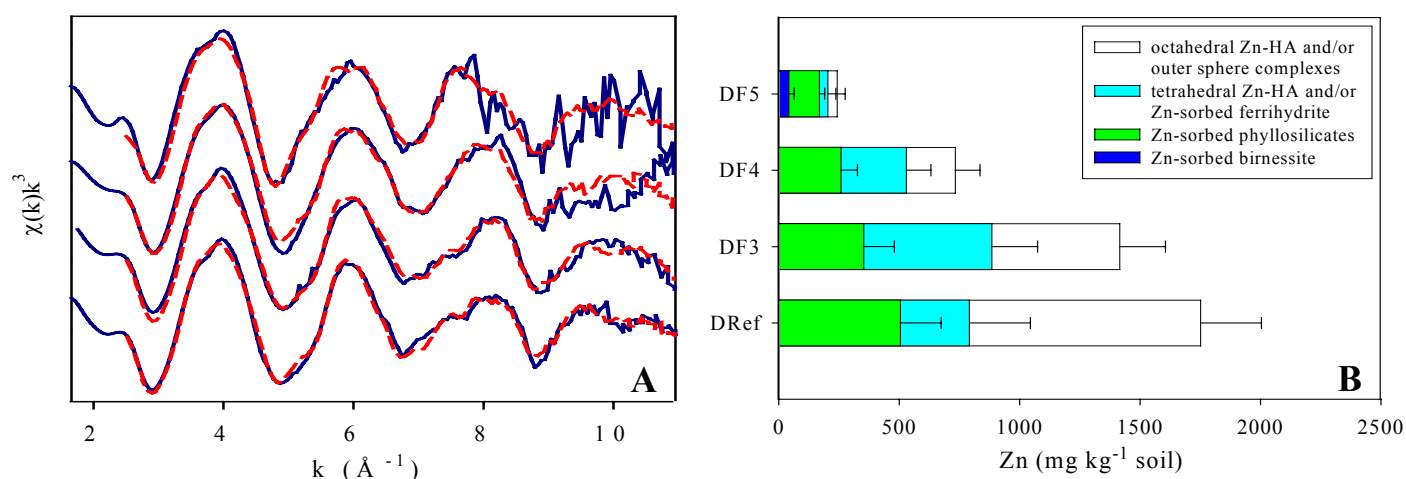


Figure 1 A) Zn K-edge EXAFS spectra (blue solid line) and fit (red dashed line) determined by LCF for the Dornach untreated reference soil (DRef) and key SSE residues. B) Distribution of Zn associated species derived from the fitted spectra.

soil results, suggest that a portion of Zn-sorbed phyllosilicates and octahedrally coordinated Zn complexes were strongly isotopically exchangeable in this highly organic smelter polluted soil.

The Mortagne untreated soil (MRef) results show that 7% of the Zn is associated with franklinite, 19% with phyllosilicates, 26 % is present as tetrahedrally coordinated complexes and 46% as octahedrally coordinated complexes (Figure 2b). The removal of Zn by F2 and F3 reagents show that the dissolution of octahedral Zn-HA and/or outer sphere complexes can be induced by NH_4 exchange with Zn (F2) and by a drop in pH (F3). As with the Dornach SSE, the increase in tetrahedrally coordinated Zn complexes is explained by the variability in the LCF method. Comparison of SA data obtained in the different fractions of the Mortagne soil suggests that octahedrally coordinated Zn complexes are the dominant Zn species involved in the most isotopically exchangeable soil fraction. On the contrary tetrahedrally coordinated Zn complexes and franklinite as well as Zn species associated with phyllosilicates (partially located within the clay lattice) undergo isotopic exchange at a slower rate or might not undergo isotopic exchange at all.

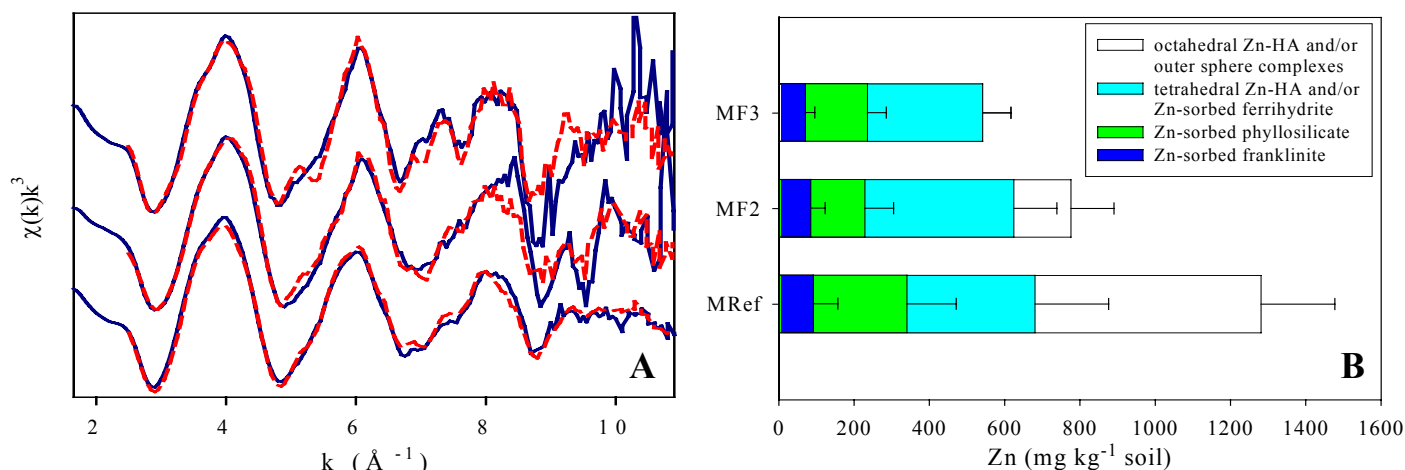


Figure 2 A) Zn K-edge EXAFS spectra (blue solid line) and fit (red dashed line) determined by LCF for the Mortagne untreated reference soil (MRef) and key SSE residues. B) Distribution of Zn associated species derived from the fitted spectra.

This combined approach of EXAFS and SSE illustrated that different Zn speciation exists between the Dornach and Mortagne exchangeable Zn pools as identified by the SSE performed on ^{65}Zn labeled soils and the IEK method during the preliminary study. Approximately 45% of the octahedrally coordinated Zn ($430 \text{ mg Zn kg}^{-1}$) was extracted from the Dornach soil during the first three extraction steps whereas the entirety of the octahedrally coordinated Zn was removed from the Mortagne soil ($600 \text{ mg Zn kg}^{-1}$) with the same extraction steps. This suggests that hydrated Zn species constituted an important part of the octahedral Zn species present in the Mortagne soil whereas a high concentration of Zn complexed on organics comprised the octahedral Zn species in the Dornach soil. Provided that the EXAFS results obtained for these two soils can be generalized to the other soils, it is hypothesized that the Zn species involved in the rapid exchange of the isotopic exchange kinetics study are primarily octahedrally coordinated Zn complexes and to a lesser extent Zn-sorbed phyllosilicates.

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Publications

Diesing W.E., Sinaj S., Sarret G., Flura T., Demaria P., Siegenthaler A., Sappin-Didier V. and Frossard E.,
The influence of soil characteristics and zinc speciation in controlling zinc isotopic exchangeability in
six heavy metal polluted soils, submitted to the *European Journal of Soil Science*

Abstract

Isotopic exchange procedures have been used extensively to estimate available Zn quantities in soils, yet further understanding of the mechanisms and factors controlling exchange and availability are limited without explicitly identifying the Zn species involved in this isotopic exchange. Six Zn polluted soils with assorted pollution sources were assessed using an isotopic exchange kinetic (IEK) technique with water and 2 mM CaCl₂ background solutions to probe the influences of pollution form on kinetic exchange parameters and exchange quantities. Using isotope labeled soils incubated for 120-days in conjunction with a selective sequential extraction (SSE), the exchangeable Zn quantities and major exchange pools were identified on the same soils. EXAFS spectroscopy was used to identify Zn forms on key extraction fractions within the most exchangeable pool of two contrasting soils. Results of the IEK show that three Zn exchange pools exist (60 minutes, 60 minutes – 14 days, beyond 14 days) in the studied soils and that the employment of a CaCl₂ background solution causes a shift of the most exchangeable pool towards the soil suspension explained by a decrease of the soil negative surface charge. With this CaCl₂ addition no difference of *E* values were noted when compared to *E* values using a water background solution. Similarly, the application of the SSE on labeled soils demonstrated the presence of three exchangeable pools for most soils with the majority exchangeable forms of Zn present in the first three extraction steps. EXAFS results confirmed this finding for the two soils examined and demonstrated that octahedrally coordinated Zn were the key species contributing to Zn exchange and potentially availability in these soils.